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Collision Lifetimes, Phase Shifts and Orbiting Phenomena

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A. Classical Functions

1. General

In the study of atomic collisions under the influence of a short-range spherically symmetric potential V(r), the phase shift plays a fundamental role. Both classical and quantal effects can be treated from this standpoint. The phase shift is intimately related to the collision lifetime, the cross section, and the deflection function.

The phase shift is equivalent classically to a function Δ that has the alternative forms:

$$\Delta(L,E) = L\pi - 2p_\infty r_o + 2\int_{r_o}^{\infty} (p(r) - p_\infty)\, dr \tag{1a}$$

$$= 2 \lim_{R\to\infty} \left\{ \int_{r_o}^{R} p(r)\, dr - \int_{b}^{R} p_o(r)\, dr \right\} \tag{1b}$$

$$= 2 \lim_{R\to\infty} \left\{ \int_{r_o}^{R} p(r)\, dr - \int_{b_1(R)}^{R} p_1(R,r)\, dr \right\} \tag{1c}$$

$$= \int_{r_o}^{\infty} p(r) \cdot \frac{r\,\frac{dV}{dr}}{E - V(r)}\, dr. \tag{1d}$$

Here the p's are radial momenta,

$$p^2(r) = 2\mu(E - V(r)) - L^2/r^2, \tag{2a}$$

$$p_o^{\,2}(r) = 2\mu E - L^2/r^2, \tag{2b}$$

$$p_1^{\,2}(R,r) = 2\mu\big(E - V(R)\big) - L^2/r^2, \tag{2c}$$

$$p_\infty^2 = 2\mu E, \quad p_R^2 = 2\mu(E - V(R)). \tag{2d}$$

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and the turning points r_o, b, and $b_1(R)$ are defined by

$$L = r_o\left[2\mu(E-V(r_o))\right]^{\frac{1}{2}} = bp_\infty = b_1(R)p_R \tag{3}$$

The connection between the Eqs. (1a) to (1d) depends on the evaluation of the integral

$$\begin{aligned} F(R) = \int_b^R p_o(R)dr &= p_\infty R(1 - \frac{b^2}{R^2})^{\frac{1}{2}} - L\frac{\pi}{2} + L\sin^{-1}(b/R) \\ &= p_\infty R - L\frac{\pi}{2} + O(\frac{b}{R}) \ldots \end{aligned} \tag{4}$$

and its replacement by a function with the same limiting behavior,

$$\begin{aligned} F'(R) &= \int_{b(R)}^R p_1(R,r)dr \\ &= p_R\left[1 - \frac{b_1^2(R)}{R^2}\right]^{\frac{1}{2}} - L\frac{\pi}{2} + L\sin^{-1}(b_1(R)/R) \\ &= L\int_1^{Rp_R/L} \frac{(x^2-1)^{\frac{1}{2}}}{x}\,dx. \end{aligned} \tag{5}$$

The final connection with Eq. (1d) comes about because

$$F'(r_o) = 0,$$

$$\frac{dF'(r)}{dr} = p(r)\left\{1 - \mu r\frac{dV}{dr}\left[2\mu(E-V(r))\right]^{-1}\right\}. \tag{6}$$

The first form of Eq. (1) is the familiar one. The second shows how the phase shift is composed of the difference between two simple action integrals, one over the radial motion on the actual trajectory and the other over the radial motion on a comparison trajectory with vanishing interaction. In the third form the comparison trajectory is taken as force-free inside R, but with the constant potential $V'(r \leq R) = V(R)$. The last form shows the contribution to the phase shift from different regions of the trajectory, displaying explicitly the dependence on the radial force $-\frac{dV}{dr}$; this form has the computational advantage of converging rapidly at large r if the interaction is of short range.

The classical deflection function is well known to be a derivative of Δ:

$$\Theta(L,E) = (\partial\Delta/\partial L)_E = \pi - 2L\int_{r_o}^{\infty} \frac{dr}{r^2\, p(r)} \tag{7a}$$

$$= 2L\int_{b}^{\infty} \frac{dr}{r^2 p_o(r)} - 2L\int_{r_o}^{\infty} \frac{dr}{r^2 p(r)} \tag{7b}$$

$$= 2 \lim_{R\to\infty} \left\{ L\int_{b_1(R)}^{R} \frac{dr}{r^2 p_1(R,r)} - L\int_{r_o}^{R} \frac{dr}{r^2 p(r)} \right\} \tag{7c}$$

$$= -L\int_{r_o}^{\infty} \frac{r\frac{dV}{dr}}{E-V(r)} \frac{dr}{r^2 p(r)} \tag{7d}$$

The last form is equivalent to one that has been used by Firsov [1] in the study of the inverse problem, the deduction of the potential from the classical deflection. Since it converges more rapidly than the first form at large r, it should be useful for computation.

The classical collision lifetime is also a derivative of Δ :

$$Q^{cl}_{coll}(L,E) = (\partial\Delta/\partial E)_L = 2\mu\int_{r_o}^{\infty}(p^{-1}(r) - p_\infty^{-1})dr - 2\mu r_o\, p_\infty^{-1} \tag{8a}$$

$$= 2\lim_{R\to\infty}\left\{\mu\int_{r_o}^{R}\frac{dr}{p(r)} - \mu\int_{b}^{R}\frac{dr}{p_o(r)}\right\} \tag{8b}$$

$$= 2\lim_{R\to\infty}\left\{\mu\int_{r_o}^{R}\frac{dr}{p(r)} - \mu\int_{b_1(R)}^{R}\frac{dr}{p_1(R,r)}\right\} \tag{8c}$$

$$= \mu\int_{r_o}^{\infty}\frac{\left(-r\,\frac{dV}{dr}\right)}{\left[E - V(r)\right]^2}\;\frac{\left[E - V(r) - L^2/\mu r^2\right]}{p(r)}\,dr. \tag{8d}$$

The last form is the preferable one for computation because of its rapid convergence. It also displays conveniently the analytical behavior of Q near the orbiting singularity and elsewhere.

The classical phase $\Delta(L,E)$ is frequently computed because of its importance for semiclassical scattering[2], which involves quantized angular momentum but ignores quantization of the radial motion. The semiclassical phase shift follows from the identifications

$$L \to (\ell + \tfrac{1}{2})\hbar,$$
$$2\hbar\,\delta_o(\ell,E) = \Delta\left\{(\ell + \tfrac{1}{2})\hbar,\ E\right\}. \tag{9}$$

$\delta_o(\ell, E)$ is just the asymptotic phase shift of the first order WKB approximate wave function. In certain cases where $\delta_o(\ell, E)$ has been tabulated for sufficiently small intervals of E it is possible to differentiate it numerically to obtain $Q^{cl}_{coll}(L,E)$.

When the potential contains a well at small r, the classical action integral for motion inside the well can always be defined:

$$A(L,E) = \int_{r_2}^{r_1} p(r)dr = \int_{r_2}^{r_1} p(r)\,\frac{r\,\frac{dV}{dr}}{E-V(r)}\,dr, \qquad (10)$$

where $r_2 < r_1$ are the turning points,† with $p(r_1) = p(r_2) = 0$; the connection between the two forms is established by the fact that the function F' of Eqs. (5) and (6) vanishes at the turning points r_2 and r_1. The function A applies as well to motion at positive energies behind a barrier (metastably bound motion) as to motion in a potential well at negative energies (truly bound motion). The function A(L,E) appears in the semiclassical approximation for the bound states in the condition

$$A\left(\left(\ell + \tfrac{1}{2}\right)\hbar,\ E^{o}_{n,\ell}\right) = \left(n + \tfrac{1}{2}\right) h \qquad (11)$$

which gives the lowest order approximation to $E_{n,\ell}$ when n is an integer. A(L,E) can obviously be looked on as a function measuring the capacity of the well, since it counts the number of bound states that can be accommodated with energies less than E.

The classical lifetime inside the well is given by the equivalent forms

$$Q^{cl}_{bound} = 2\mu\int_{r_2}^{r_1}\frac{dr}{p(r)}$$

$$= \mu\int_{r_2}^{r_1}(-r\,\frac{dV}{dr})\left[E - V(r)\right]^{-2}\left[E - V(r) - L^2/\mu r^2\right]\frac{dr}{p(r)} \quad .(12)$$

This obviously is just the time taken for one complete cycle of motion in the well. The total classical lifetime,

$$Q^{cl}_{tot}(E,L) = Q^{cl}_{coll} + Q^{cl}_{bound}, \qquad (13)$$

† I shall use the convention of indexing the turning points odd when the radial force is positive, and even when it is negative, with the indices increasing as r decreases.

is more than just a formal construct -- it is the natural expression to use in discussing the thermodynamic properties of the gas. The internal partition function for diner clusters is conveniently expressed[3] in a form whose classical limit is

$$Q_{cl}^{int} = h^{-1}\iint e^{-E/kT} Q_{tot}^{cl}(E,L)\, dE\, d(L^2/K^2). \tag{14}$$

Closely related to the classical action integrals is the integral

$$B(L,E) = 2\int_{r_1}^{r_o} |\, p(r)\,|\, dr \tag{15}$$

which measures the imaginary action for motion in the classically forbidden region under a barrier. This integral appears in the lowest order approximation for the quantal barrier leakage.

2. Orbiting

Whenever the effective potential,

$$U(r) = V(r) + L^2/2\mu r^2, \tag{16}$$

has a smooth maximum, classical orbiting will occur at energies near the energy E_m of the maximum. The classical collision lifetime has a logarithmic singularity as $E \to E_m$ from below and above, and the classical phase Δ suffers a discontinuous step by the amount $A(L,E_o)$ given by Eq. (10). Ford, Hill, Wakano and Wheeler[4] have given a valuable analysis of these discontinuities at orbiting, and have shown that they are artifacts of the classical approximation which disappear when quantum mechanics is applied. In this they are reminiscent of the classical infinity in the total scattering cross section, which only disappears in quantum mechanics (see especially the recent work of Pauly[5]).

Orbiting collisions are expected to play an important role in the 3-body study recombination of reactive atoms. Several classical treatments of such events are already available.[6] The most important states contributing in such theories are presumably the long-lived collisions at energies close to orbiting. This is just the region where the quantal correction to the classical infinity must come in, and its importance must be evaluated. Before going on to an examination of the quantal approximations, it is convenient here to examine the properties of some simple potentials that illustrate the behavior of the classical collision lifetime.

a. Parabolic Barrier

The simplest potential that exhibits the orbiting phenomenon is the quadratic,

$$V_o = E_m - \frac{a}{2}(x - x_m)^2. \tag{17}$$

While this potential cannot be valid over the whole range of r, it is almost always a good approximation within some distance d of the maximum. When the energy E of the motion is close to E_o,

$$E = E_o + \mathcal{E}, \tag{18}$$

the contribution to the classical lifetime from the motion in the region $x_m \leq x \leq x_m + d$ can be computed. It is

$$Q_o^{cl}(d) = 2(\mu/a)^{\frac{1}{2}} \ell n \left\{ \xi_1 + (\xi_1^2 \pm 1)^{\frac{1}{2}} \right\} - d(2\mu/(E + \mathcal{E}))^{\frac{1}{2}}, \tag{19}$$

where

$$\xi_1^2 = ad^2/2|\mathcal{E}| \tag{20}$$

and the sign ($\pm$) is taken in the same sense as the sign of $\mathcal{E}$. When $\mathcal{E}$ is small Eq. (19) can be expanded to give

$$Q_o^{cl}(d) = (\mu/a)^{\frac{1}{2}} \left\{ \ell n\,(2ad^2/|\mathcal{E}|) + \frac{\mathcal{E}}{ad^2} \ldots \right\} - d(2\mu/(E + \mathcal{E}))^{\frac{1}{2}}. \tag{21}$$

This expression exhibits the logarithmic singularity of Q^{cl} as $\mathcal{E} \to 0$. When Eq. (19) or (21) is applied in the radial orbiting problem, the expression for $Q_o^{cl}(d)$ must be doubled when $\mathcal{E} > 0$, in order to take proper account of the motion in the full region $x_m - d \leq x \leq x_m + d$.

B. Attractive Power Law

More realistic for the atomic collision problem is the pure radial attractive potential,

$$V_\perp(n) = -a_n r^{-n} \quad (n > 2). \tag{22}$$

This must of course be coupled with the centrifugal term,

$$u = L^2/2\mu r^2, \tag{23}$$

to show the orbiting maximum. The resulting effective potential can be written in a form that scales conveniently,

$$\mathcal{V}_1(n) = A\,(V_1 + u) = -\rho^{-n} + \rho^{-2}, \tag{24}$$

where

$$A = (2\mu/L^2)(2\mu a_n/L^2)^{2/n-2},$$

$$\rho = r/r_*, \qquad = r_* = (2\mu a_n/L^2)^{1/n-2}. \tag{25}$$

The maximum occurs at

$$\rho_m = (n/2)^{1/n-2} \text{ with } \mathcal{V}_1(\rho_m) = \frac{n-2}{n}\,(2/n)^{2/n-2}$$

and

$$\mathcal{V}_1''(\rho_m) = -2(n-2)(2/n)^{4/n-2}. \tag{26}$$

The inflection point occurs at

$$\rho_{inf} = (n(n+1)/6)^{1/n-2}$$

with

$$\mathcal{V}_1(\rho_{inf}) = \frac{(n-2)(n+3)}{n(n+1)}\left(\frac{6}{n(n+1)}\right)^{2/n-2} = \mathcal{V}_1(\rho_m)\,\frac{n+3}{n+1}\left(\frac{3}{n+1}\right)^{2/n-2}$$

and

$$\mathcal{V}_1'(\rho_{inf}) = \frac{-2(n-2)}{n+1}\left(\frac{6}{n(n+1)}\right)^{3/n-2}. \tag{27}$$

From Eq. (26) we see that the quadratic approximation to the maximum, Eq. (17), is characterized by the constants

$$a = -(Ar_*^2)^{-1} \mathcal{V}_1''(\rho_m) = \frac{(n-2)L^2}{\mu}\left(\frac{L^2}{n\mu a_n}\right)^{4/n-2}$$

and
$$E_m = \mathcal{V}_1(\rho_m)/A = \frac{(n-2)L^2}{2n\mu}\left(\frac{L^2}{n\mu a_n}\right)^{2/n-2} \tag{28}$$

The distance d in Eqs. (19) to (21) should obviously be taken somewhat less than the distance d_{inf} from the inflection point to the maximum,

$$d_{inf} = r_*(\rho_{inf} - \rho_m)$$
$$= \left(\frac{n\mu a_n}{L^2}\right)^{1/n-2}\left[\left(\frac{n+1}{3}\right)^{1/n-2} - 1\right]. \tag{29}$$

From the potential $\mathcal{V}_1(n)$ we can also determine the form of the collision lifetime in the low energy limit at finite L. Using Eq. (6d) and making the turning point ρ_o the principal parameter, one can define

$$s = \rho_o/\rho,$$
$$\epsilon = AE = -\rho_o^{-n} + \rho_o^{-2} \tag{30}$$
$$\epsilon = \rho_o^{-n+2}$$

so that
$$Q^{cl}/(2\mu A)^{\frac{1}{2}} r_* = n\rho_o^{-n+4}\int_o^1 \frac{s^{n-2}(2s^2-1)\left[1 + g\left(\frac{1-s^n}{2s^2-1}\right)\right]ds}{(1-s^2)^{\frac{1}{2}}\left[1 - g(1-s^7)\right]^2\left[1 - g\left(\frac{1-s^n}{1-s^2}\right)\right]^{\frac{1}{2}}}$$
$$= n\rho_o^{n+4}\sum_{j=0}^{\infty} g^j I_j(n). \tag{31}$$

The last form represents an expansion of the integral in powers of ϵ, valid at small ϵ or small L. Inverting Eq. (30) we find

$$\rho_o = \epsilon^{-\frac{1}{2}} - \frac{1}{2}\epsilon^{(n-3)/2} \ldots$$

$$E = \epsilon^{\left(\frac{n}{2}-1\right)} + \ldots , \qquad (32)$$

so that convergence is assured if $n \geq 3$. Eq. (31) can then be rearranged as an expansion in powers of ϵ. The leading term gives

$$q^{cl} = (2\mu/L^2)^{n/2} \; L \; a_n \; E^{(n-4)/2} \; n \; I_o(n) \ldots\ldots \qquad (33)$$

The integrals $I_o(n)$ can be evaluated easily:

$$I_o(3) = \tfrac{1}{2},\ I_o(4) = \frac{\pi}{4},\ I_o(5) = 1,\ I_o(6) = \frac{3\pi}{8}. \qquad (34)$$

c. Lennard-Jones Potential

For this case the potential $V_2(r)$ is usually expressed in terms of the well depth ϵ and the turning point r_o^o at E = L = 0:

$$V_2 = 4\epsilon\left\{(r/r_o^o)^{-12} - (r/r_o^o)^{-6}\right\}. \qquad (35)$$

To discuss the orbiting maximum it is possible to write the equation in a reduced form similar to that of the preceding section:

$$\nu_2 = A(V_2 + u) = \beta\rho^{-12} - \rho^{-6} + \rho^{-2}, \qquad (36)$$

where

$$\beta = (2\mu)^{\frac{1}{2}} 2^{-5} L^3 \varepsilon / \mu^2. \tag{37}$$

However, we shall use instead the dimensionless form

$$v_2 = U_2/4\varepsilon = s^{-12} - s^{-6} + \gamma s^{-2}, \tag{38}$$

with

$$s = r/r_o^o = r_* \rho / r_o^o, \qquad \gamma = L^2/8\mu\varepsilon(r_o^o)^2. \tag{39}$$

The maximum of v_2 occurs at s_{2m}, where

$$\gamma = 3s_{2m}^{-4} - 6\, s_{2m}^{-10}$$

$$s_{2m} = \left(\frac{3}{\gamma}\right)^{\frac{1}{4}} \left(1 - \tfrac{1}{2}\left(\frac{\gamma}{3}\right)^{3/2} \ldots.\right) \tag{40}$$

and the value of v_2 at the maximum is

$$v_2(m) = 2\, s_{2m}^{-6} - 5\, s_{2m}^{-12} = 2\left(\frac{\gamma}{3}\right)^{3/2} + (\gamma/3)^3 \ldots\ldots \tag{41}$$

The second derivative at the maximum is

$$v_2''(m) = -24\, s_{2m}^{-8} + 120\, s_{2m}^{-14} = \frac{8\gamma^2}{3}\left(1 - (\gamma/3)^{3/2} \ldots\right). \tag{42}$$

The maximum merges with the minimum behind the barrier at the critical values

$$\gamma^\dagger = \frac{9}{25} 5^{1/3}, \; s^\dagger = 5^{1/6}, \; v_2(s^\dagger) = 1/5, \; v_2''(s^\dagger) = 0. \tag{43}$$

By comparison with the simpler function

$$v_1 = -s^{-6} + \gamma s^{-2} = \nu_1(6)/4\varepsilon A, \tag{44}$$

for which

$$s_{1m} = (3/\gamma)^{\frac{1}{4}},\ v_1(m) = 2\, s_{1m}^{-6} = 2(\gamma/3)^{3/2},$$

$$v_1''(m) = 24\, s_{1m}^{-8} = -8\gamma^2/3, \tag{45}$$

it is seen that the short-range repulsion moves the maximum to smaller r and raises it slightly. However, the deviation from the behavior of the comparison function v_1 is not great until quite close to the critical values $\gamma^\dagger$, $s^\dagger$. For most purposes connected with orbiting at energies and angular momenta below the critical values it is therefore quite valid to neglect the repulsive part of the potential, at least for a semiquantitative survey of the behavior. It is worth noting that the critical energy for the Lennard-Jones potential is 4/5 of the dissociation energy.

B. Quantal Collisions

1. Semiquantitative Survey.

a. General

The scattering matrix $\underline{S}$ provides the most familiar general formulation of quantal collision problems. In many cases, at least over a restricted energy range, it suffices to consider single channels separately and the computation reduces to the determination of phase shifts $\delta_\ell(E)$, with the relationship

$$S_{\ell\ell} = e^{2i\delta_\ell}. \tag{46}$$

The lifetime matrix is related to S by the matrix equation

$$\underset{\sim}{Q} = i\hbar \underset{\sim}{S}\, d\underset{\sim}{S}^{\dagger}/dE. \tag{47}$$

In the single channel case this reduces to

$$Q_{\ell\ell}(E) = 2\hbar d\delta_{\ell}/dE. \tag{48}$$

Both the scattering and lifetime matrices can be applied to many-body collisions.

b. Bound States.

The lifetime matrix can be defined even in the energy region where only bound states exist. A typical diagonal element $Q_{ii}(E)$ there shows a spectrum of narrow resonances that may be represented as δ-functions or as peaks centered at E_i with a finite half-width Γ_i determined by the radiative transition probabilities (or other interactions). Near E_i, then,

$$Q_{ii}(E) = \hbar\, \Gamma_i \left[(E_i-E)^2 + (\Gamma_i/2)^2\right]^{-1} \equiv q(\Gamma_i, E_i-E). \tag{49}$$

The probability of observing the specific energy E, if it is known that the system is in the state i, is

$$P_i(E) = Q_{ii}(E)/h, \tag{50}$$

and the integral over the resonance region gives

$$\int_{\text{resonance}} Q_{ii}(E)dE = h. \tag{51}$$

It is now possible to invert Eq. (48) and define the phase shift unambiguously

even for the bound region of the spectrum:

$$2\hbar\,\delta_\ell(E) = \int_{-\infty}^{E} Q\,\alpha(E')dE'. \tag{52}$$

The phase shift in the bound region has, by virtue of Eq. (49), a step of magnitude π at each bound level E_i; these steps are rounded in accordance with the respective widths Γ_i:

$$\delta_\ell(E) = \delta_\ell(E \ll E_i) + \frac{\pi}{2} + \tan^{-1}(\Gamma_i/2(E_i - E)). \tag{53}$$

The phase shift at zero energy then automatically satisfies Levinson's theorem,

$$\delta_\ell(0) = N_\ell \pi, \tag{54}$$

where N_ℓ represents the number of bound states. More generally,

$$\delta_\ell(E) = \pi n_\ell(E), \tag{55}$$

where $n_\ell(E)$ is the number of bound states with energies below E ($E \geq 0$). These equations are valid for states of any angular momentum.

For more complicated systems where simple phase shifts may be hard to define, Eq. (47) can be inverted to define the S-matrix through an integral equation:

$$\underline{S}(E) = \underline{1} + i\hbar^{-1}\int_{-\infty}^{E} \underline{Q}\underline{S}(E')\,dE'. \tag{56}$$

By this equation the phases of $\underline{S}$ are uniquely defined in a way that should satisfy a generalized Levinson's theorem.

c. Barriers and Semi-bound States.

Equations (52) and (56) are of course valid at any energy, not merely in the bound region. Let us now look in particular at the effect of the semi-bound region behind a potential barrier (most commonly of centrifugal origin) in a scattering problem. In the classical limit, motion in this region becomes fully bound, and it is very nearly so for heavy masses and thick barriers in quantum mechanics. A characteristic dimensionless parameter, for a potential of standard shape, can be written in terms of the energy minimum $-\mathcal{E}$ and the turning point r_o^o at E = 0, L = 0:

$$\hbar = \hbar / (2\mu\mathcal{E})^{\frac{1}{2}} r_o^o. \tag{57}$$

The classical limit is approached as $\hbar \to 0$. As long as $\hbar$ is small and the energy E is far enough below the top of the barrier at E_m, the system is in the semiclassical region where the semi-bound states can be treated very well by the first-order WKB approximation. The region near the top of the barrier requires separate attention, and will be discussed in the next section.

In the semiclassical region, where barrier penetration is small, the semi-bound states are characterized principally by their energy level, $E_{\ell,n}$ and their width $\Gamma_{\ell,n}$. In the simplest form of the WKB approximation, the energy levels of both bound and semi-bound states are determined by Eq. (11); the dependence on the parameter $\hbar$ is shown by rewriting this in terms of reduced quantities:

$$\gamma = E/\mathcal{E}, \quad \rho = r/r^o$$
$$\alpha(\gamma) = A r_o^{o-1} (2\mu\mathcal{E})^{-\frac{1}{2}} = 2\int_{\rho_2}^{\rho_1} (\gamma - U/\mathcal{E})^{\frac{1}{2}} d\rho,$$
$$\alpha(\gamma_{\ell,n}) = 2\pi\hbar(n + \tfrac{1}{2}). \tag{58}$$

The average density of energy levels near E is then given approximately by

$$\rho^{o}(E,\rho) = \left(\frac{dn}{dE}\right)_{o} = \frac{1}{2\pi\hbar\Sigma}\frac{\partial\alpha}{\partial y} = h^{-1}Q^{cl}_{bound}. \tag{59}$$

(This is a special case of a general relation between the density of levels and the lifetime.) The shape of the resonance level is still given approximately by Eq. (49), but the level widths $\Gamma_{\ell,n}$ are now determined not only by radiative processes but also by the transmission of the barrier. The quantal lifetime spectrum can be subdivided approximately into an internal part embodying these resonances,

$$Q_{int}(E,\ell) \approx \sum_{n} q(\Gamma_{\ell,n}, (E_{\ell,n} - E)) \quad (E \ll E_{m}), \tag{60}$$

and on external part Q_{ext} that is given in first approximation by the classical formula Q^{cl}_{coll} of Eq. (8). The classical lifetime Q^{cl}_{bound} represents essentially the average behavior of the function Q_{int} of Eq. (60). The true quantum lifetime function cannot strictly be divided into external and internal parts, but in the semiclassical region it can be approximated very well by the sum of these two:

$$Q(\ ,E) \approx Q_{int}(E,\ell) + Q^{cl}_{coll}(E,\ell), \ (E \ll E_{m}). \tag{61}$$

The behavior of the phase shift can now be examined by extending Eq. (52) into the semiclassical region. The phase shift here continues to show a slightly rounded step of magnitude π every time a resonance level is passed, which we can attribute to the internal contribution to the phase shift:

$$\delta_{\ell}^{int}(E) \approx \frac{\pi}{2} + \sum_{n} \tan^{-1}(\Gamma_{\ell,n}/2(E_{\ell,n} - E)). \tag{62}$$

This step function is now superimposed on a gradually shifting background $\delta_\ell^{ext}(E)$ due to the external part of the potential which is approximately given by the function $\delta_o(\ell, E)$ of Eq. (9). The average behavior of the internal step function is represented by the function A(L,E) of Eq. (10).

The level widths in the semiclassical region are affected by the possibility of penetration through the barrier as well as by radiative and other interactions. I shall consider here only the barrier penetration contribution, which for simplicity of notation will be denoted just $\Gamma_{\ell,n}$. The reciprocal of the average lifetime of the level (ℓ, n) depends on the product of the frequency of collision with the barrier, approximately $1/Q^{cl}_{bound}(E_{n,\ell})$, and the barrier transition probability, which is $\exp(-B(\ell,E)/\hbar)$, according to the simple WKB result, with B given by Eq. (15). The dependence on the parameter is shown if we write

$$\beta(\ell,\gamma) = Br_m^{-1}\ (2\mu\mathcal{E})^{-\frac{1}{2}} = 2\int_{\rho_1}^{\rho_o} (-\gamma + U/\mathcal{E})^{\frac{1}{2}}\, d\rho. \tag{63}$$

Then the average lifetime of the $n^{\underline{th}}$ level is given by

$$\overline{\tau}(\ell, n) = 2\hbar/\Gamma_{\ell,n} \simeq Q^{cl}_{bound}(E_{n,\ell})\ \exp(B(\ell,E_{n,\ell})/\hbar), \tag{64}$$

or

$$\Gamma_{\ell,n} \tfrac{1}{2} = \hbar\,\mathcal{E}(\partial\alpha/\partial\gamma)^{-1}\ \exp(-\beta(\ell,\gamma)/\hbar). \tag{65}$$

From these expressions we can derive an estimate of the average rate of penetration through the potential barrier in an energy range ΔE embracing several resonance levels. In the time Δt and the range ΔE the number of barrier passage events ΔN is proportional to the density of available levels multiplied by the reciprocal of the average lifetime, with an additional factor of $\frac{1}{2}$ for

passage in one direction only. The result, from Eqs. (59) and (64), is

$$\Delta N \simeq \tfrac{1}{2}\hbar^{-1}\Delta E \Delta t \exp(-B(\ell,E)/\hbar). \tag{66}$$

In the approach to the classical limit the density of energy levels increases linearly with $\hbar^{-1}$, while the level widths Γ_i and the rate of barrier passage decrease exponentially with $\hbar^{-1}$. Thus the barrier rapidly becomes impenetrable. More interesting is the fact that the levels become exponentially more and more isolated from each other even as they approach the classical infinite density. The classical spectrum is therefore not a simple continuum, but rather an infinitesimal fine-toothed comb. The usual continuous classical expressions are not the result of a simple passage to the limit $\hbar \to 0$, but they require an averaging as well.

The pathological nature of the classical spectrum, with infinite δ-function discontinuities at every point, is, naturally, only imperfectly represented by the classical expressions $Q^{cl}(L,E)$ and $\Delta(L,E)$. Similarly, when $\hbar$ is small but finite, it is hopeless to try to represent the behavior of the resonances by using the WKB expansion of the phase shift or the lifetime in powers of $\hbar$ beginning with the classical term. One must expect such an expansion to miss the resonances completely. That expansion may nevertheless be useful in improving the background continuous spectrum attributable to the external parts Q^{ext} or ε^{ext} that depend mainly on the potential near the outer turning point.

By using refinements of the WKB method which do not necessarily depend on a simple expansion in $\hbar$, it is of course possible to improve on the estimates of the energy level positions and widths given here. Some attention will be given to such improvements later in this paper.

d. Behavior Near a Barrier Maximum

Close to the maximum, it is natural to approximate the barrier by a parabola. Quantal effects in such a region have been frequently studied, perhaps most carefully by Ford, Hill, Wakano and Wheeler.[4] The characteristic circular frequency ω_o plays a fundamental role in the theory -- it is just the frequency that would be associated with the harmonic oscillator if the parabola were inverted. In the notation of Eq. (17), ω_o is defined by

$$\omega_o = (a/\mu)^{\frac{1}{2}}. \tag{67}$$

For atomic collisions we can use the potential v_1 of Eq. (44), with γ and ϵ given by Eqs. (39) and (57) and a dimensionless quantity containing ω_o,

$$\hbar\omega_o/4\epsilon = (2/3^{\frac{1}{2}})\epsilon^{\frac{1}{2}}\gamma, \tag{68}$$

where we can also express γ in the form

$$\gamma = \hbar^2 l(l+1)/4 \doteq \hbar^2 (l+\tfrac{1}{2})^2/4. \tag{69}$$

The quantity $\hbar\omega_o$ is a natural measure of the energy range near the barrier maximum in which quantal effects must dominate; comparing this with the height of the maximum we get the ratio

$$\hbar\omega_o/U_1(\max) = 3\epsilon/\gamma^{\frac{1}{2}} = 6/[l(l+1)]^{\frac{1}{2}} \doteq 6/(l+\tfrac{1}{2}). \tag{70}$$

This criterion, independent of mass, shows that barrier maximum effects may be important throughout the whole of the barrier for values of the angular momentum

quantum number less than about 6 -- but the barrier is far from parabolic in most of this region, so a more refined theory is called for.

A related criterion can be used to estimate the importance of the region of quantal behavior as it depends on the reduced mass and other parameters of the system. If we plot the locus of the maximum in a diagram of energy versus L^2, or of $E/4\varepsilon$ versus γ, we obtain, by Eq. (45), the curve

$$E_m/4\varepsilon = 2(\gamma/3)^{3/2}. \tag{71}$$

The region of strong quantal behavior can be shown bracketing this curve at a distance

$$\Delta E/4\varepsilon = \pm\hbar\omega_o/4\varepsilon = \pm(2/3^{\frac{1}{2}})\ell\gamma. \tag{72}$$

The temperature can be shown on the same diagram as a horizontal line $kT/4\varepsilon$. Finally a limit in γ can be introduced beyond which the interaction can be ignored. The relative importance of the quantal behavior can then be estimated from the relative areas of the quantal and classical parts of the diagram (by plotting L^2 or γ, the multiplicity associated with L is properly taken into account). By using the new reduced quantities

$$\begin{aligned} z &= \gamma/9\, H'^2, \\ w_\pm = w_o \pm \Delta w &= \frac{E_m \pm \Delta E}{8\cdot 3^{3/2}\ell'^3\varepsilon} = z^{3/2} \pm z, \\ w_T &= \frac{kT}{8\cdot 3^{3/2}\ell'^3\varepsilon} = z_T^{3/2}, \end{aligned} \tag{73}$$

we arrive at a single reduced diagram.

We can now compare the areas

$$I_{qu} = 2\int_0^{z_T} \Delta w \, dz = w_T^{4/3}$$

and

$$I_{tot} = w_T z_T = w_T^{5/3},$$

forming the ratio

$$R = I_{qu}/I_{tot} = w_T^{-1/3} = 2\cdot 3^{\frac{1}{2}} \hbar'(\mathcal{E}/kT)^{1/3}. \qquad (74)$$

Since the areas are proportional to volumes in phase space, the ratio R is a satisfactory measure of the importance of the quantal region at the temperature T. In Table I this procedure is applied to some representative cases.

The characteristic frequency ω_o plays an important role in the quantum effect that damps out the logarithmic singularity in the classical lifetime spectrum at the orbiting energy. It is possible to use simple uncertainty principle arguments to show that the maximum of the classical curve must be limited to about ω_o^{-1} (the quantal resonances superposed on this curve are much higher, but narrow in proportion). These results are substantiated by the more detailed theory of Ford, Hill, Wakano and Wheeler.[4] Taking $z = (e - E_m)/\hbar\omega_o$, their formula for the external part of the phase shift (which omits the contribution of the resonances) leads to the result for Q_{ext} when z is small:

$$Q_{ext} = \frac{2}{\omega_o}\frac{d\sigma_{ext}}{dz} = \frac{1}{\omega_o}\left\{-\tfrac{1}{2}\ell n\left[\left(\frac{z}{e}\right)^2 + \left(\frac{1}{4\gamma}\right)^2\right] - \left[1 + \left(\frac{e}{4\gamma z}\right)^2\right]^{-1} + \frac{\pi e^{\pi z}}{1 + e^{2\pi z}}\right\}, \qquad (75)$$

where $\gamma = 1.7811$ is Euler's constant; this gives the quantal limitation on the classical orbiting singularity:

$$Q_{ext} \leq \omega^{-1}\ell n(4\gamma) = 1.964\,\omega_o^{-1}. \tag{76}$$

Their theory also describes the important phenomena associated with the modification of the quantal resonances near the barrier maximum. However, they do not explicitly discuss the related effect of virtual levels immediately above the classical maximum. Qualitatively, their theory shows that the resonances behind the barrier continue to play a role right up to the maximum, but are much broadened and distorted in shape.

The barrier penetration probability deviates from the simple form $e^{-B/\hbar}$, becoming

$$(e^{B/\hbar} + 1)^{-1}, \tag{77}$$

a result that is exact for a parabolic barrier and probably a good approximation even where the shape diverges from the parabola. In what follows we shall review and extend their treatment, applying the theory in some detail to some atomic collision cases. In the case of H + H collisions we shall be able to compare the approximate theory with some illuminating exact computations.

Particularly in cases where γ is small, it appears from Eq. (71) that the domain of strong quantal behavior extends over a much wider energy range than the parabolic approximation is valid. In fact, the parabolic approximation cannot extend as far as the inflection point, and we have by Eq. (27),

$$1 - E_{infl}/E_{max} = 1 - \frac{9}{7}\left(\frac{3}{7}\right)^{\frac{1}{2}} = 0.158. \tag{78}$$

By comparison with Eq. (71), we see that quite large values of ℓ are required before the quantal region is safely confined to the parabolic region. The criterion is

$$\hbar\omega_o/(E_{max} - E_{infl}) = 6/0.158\,(\ell + \tfrac{1}{2}) = 37.9/(\ell + \tfrac{1}{2}) \ll 1. \qquad (79)$$

Furthermore, the treatment of Wheeler et al.[4] is accomplished by matching the solution appropriate to the parabola immediately to a WKB solution at some intermediate distance. This implies that the WKB solution must be valid to a radius at least as small as the inflection point. However, this can be tested by using the criterion given by Schiff,[7] that

$$\left| \frac{1}{2k^2} \frac{dk}{dr} \right| = \left| \frac{-\hbar\, d\,U/dr}{2\{2\mu(E-U(r))\}^{3/2}} \right| \ll 1 \qquad (80)$$

if the WKB solution is to be valid. In the special case $E = E_{max}$, $r = r_{infl}$ this reduces to

$$\left(\frac{12}{7}\right)^{3/4} \cdot (0.158)^{-3/2} \cdot (\ell + \tfrac{1}{2})^{-1} = 23.8/(\ell + \tfrac{1}{2}) \ll 1. \qquad (81)$$

This again requires very large values of ℓ for validity.

Fortunately, it is possible to develop a quantitative method of approximation valid for small values of ℓ and energies near the barrier maximum by using the technique of Miller and Good.[3] Their results show that Eq. (77) is valid even where the potential is no longer parabolic. In the next section we shall apply Miller and Good's method to extend the results of Wheeler et al. This method proves valid for H + H collisions, and can easily be applied to heavier atoms for which it must be even more reliable.

In Table I we give some numerical estimates of the importance of orbiting quantal effects for some diatomic collisions chosen throughout the periodic table. These are necessarily imprecise, principally for the reason that the strength of

the long range attraction which controls the orbiting behavior is not experimentally known. Accordingly we have used the experimentally known dissociation energies and equilibrium distances with the Lennard-Jones equation. Besides the dimensionless quantities of Eq. (57) and R_{2930} of Eq. (74), we give the reciprocal of the frequency $\omega_o(\ell = 1)$ which limits the magnitude of the classical maximum in the lifetime at orbiting. The corresponding limit for other values of ℓ can be obtained from the equation

$$\omega_o^{-1}(\ell) = \frac{3^{\frac{1}{2}}}{2\xi k^3} \cdot \frac{1}{\ell(\ell+1)} = \frac{2}{\ell(\ell+1)}\ \omega_o^{-1}(\ell = 1). \tag{82}$$

From Eq. (70) we get also

$$E_{max}(\ell) = \frac{k}{6}\left\{\ell(\ell+1)\right\}^{\frac{1}{2}}\omega_o(\ell) = \frac{\hbar}{12}\left\{\ell(\ell+1)\right\}^{\frac{1}{2}}\omega_o(\ell = 1) = \left[\ell(\ell+1)/2\right]^{3/2} E_m(\ell = 1). \tag{83}$$

It appears in Table I that the statistical criterion R, measuring the importance of the quantal orbiting region of phase space, falls off much more slowly than $\hbar$. Quantal effects may thus be of importance in transport properties and three-body reactions of atoms, at least throughout the first row elements including the atmospheric gases O and N.

Table I

	$E_{diss.}$ eV	$10^8 r_{eq}$ cm	2μ AMU		R_{293°	$\omega_o^{-1}(\ell = 1)$ sec
H_2	4.476	.7417	1.008	.0461	.896	6.537×10^{-13}
OH	4.35	.971	1.897	.0260	.502	3.74×10^{-12}
Li_2	1.03	2.672	7.018	.0101	.1205	2.70×10^{-10}
N_2	9.756	1.094	14.007	.00776	.1960	6.26×10^{-11}
O_2	5.080	1.207	16	.00667	.1355	1.897×10^{-10}
Cl_2	2.475	1.988	34.98	.00392	.0627	1.912×10^{-9}
Br_2	1.971	2.284	79.94	.00253	.0375	8.955×10^{-9}
I_2	1.542	2.666	126.93	.00195	.0266	2.512×10^{-8}

Notes and References

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